PATENT ABSTRACTS OF JAPAN

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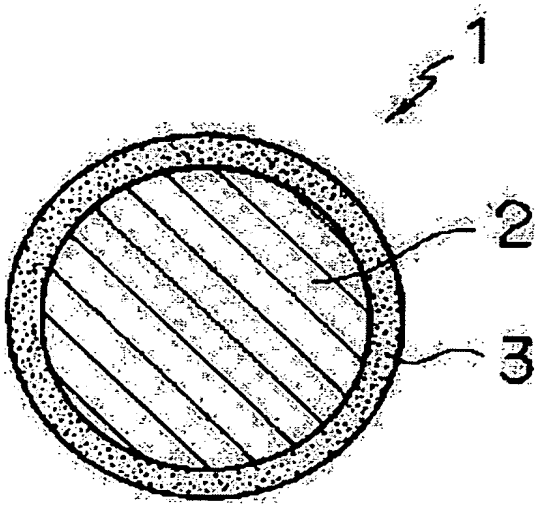
(54) RED LIGHT-EMITTING PHOSPHOR AND LIGHT-EMITTING APPARATUS USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a red light-emitting phosphor with which a red light can be efficiently obtained when activated with a long-wavelength UV light, etc., characteristics of La2O2S:Eu, Sm phosphor (red light-emitting phosphor) are utilized, agglomeration caused by moisture absorption, etc., in storage is prevented and an excellent dispersibility is retained for a long period of time.
SOLUTION: This red light-emitting phosphor 1 is obtained by sticking the surface of a phosphor particle 2 composed of lanthanum oxysulfide phosphor ((La1-x-yEuxSmy)2O2S (0.01≤x≤0.15, 0.0001≤y≤0.03) activated by trivalent europium and samarium with a metal oxide to form a moistureproof layer 3. An oxide containing at least one kind selected from Al, Si, Y, Gd, Lu, Ti, Nb, Ta and Zn is used as the moistureproof layer 3. The metal oxide in the mass ratio to the phosphor particle 2 in the range of 0.01-5% is stuck to the particle.



CLAIMS

[Claim(s)]
[Claim 1]A red light fluorescent substance comprising:

A fluorescent substance particle which consists of an acid lanthanum sulfide fluorescent substance activated with trivalent europium and samarium.
A damp proof course which consists of a metallic oxide to which the surface of said fluorescent substance particle adhered.

[Claim 2]In the red light fluorescent substance according to claim 1, said acid lanthanum sulfide fluorescent substance, A general formula: $(La_{1-x-y}Eu_xSm_y)$ A red light fluorescent substance having the presentation expressed with $_2O_2S$ (the inside of a formula, and x and y are $0.01<=x<=0.15$ and a number with which it is satisfied of $0.0001<=y<=0.03$, respectively).
[Claim 3]A red light fluorescent substance characterized by said metallic oxide being an oxide containing at least one sort of metallic elements chosen from aluminum, Si, Y, Gd, Lu, Ti, Nb, Ta, and Zn in the red light fluorescent substance according to claim 1 or 2.
[Claim 4]A red light fluorescent substance adhering to said metallic oxide in 0.01 to 5% of range in a mass ratio to said fluorescent substance particle in a red light fluorescent substance of claim 1 thru/or claim 3 given in any 1 paragraph.
[Claim 5]A red light fluorescent substance, wherein said acid lanthanum sulfide fluorescent substance is replaced in a red light fluorescent substance of claim 1 thru/or claim 4 given in any 1 paragraph by at least one sort as which less than 30mol% of La is chosen from Y and Gd.
[Claim 6]A red light fluorescent substance when said acid lanthanum sulfide fluorescent substance is excited by ultraviolet rays with a wavelength of 270-395 nm in a red light fluorescent substance of claim 1 thru/or claim 5 given in any 1 paragraph, wherein it emits light in red light.
[Claim 7]A red light fluorescent substance when said acid lanthanum sulfide fluorescent substance is excited by ultraviolet A with a wavelength of 350-390 nm in a red light fluorescent substance of claim 1 thru/or claim 5 given in any 1 paragraph, wherein it emits light in red light.
[Claim 8]A luminescent device comprising:
A light source which emits ultraviolet rays.
A light-emitting part which has a fluorescent substance for luminescent devices which is excited by ultraviolet rays from said light source, and makes visible light emit light, including a red light fluorescent substance of claim 1 thru/or claim 5 given in any 1 paragraph.

[Claim 9]A luminescent device which adds said fluorescent substance for luminescent devices to said red light fluorescent substance in the luminescent device according to claim 8, and is characterized by including a blue light fluorescent substance and a green emission fluorescent substance.
[Claim 10]A luminescent device characterized by said luminescent device being a LED lamp possessing a light emitting chip which has a nitride based compound semiconductor layer which emits ultraviolet A with a wavelength of 350-390 nm as said light source in the luminescent device according to claim 8 or 9.

[Translation done.]

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the red light fluorescent substance used for luminescent devices, such as a LED lamp, and the luminescent device using it.
[0002]
[Description of the Prior Art]The LED lamp using a light emitting diode (LED) is used for various displays, such as a light source for a portable device, a PC peripheral, OA equipment, various switches, and back lights, and the plotting board. Since a LED tip is a semiconductor device, it is long lasting, and is reliable, and the application to various uses [reduce / when it uses as a light source / the clearing work] is tried.
[0003]When applying a LED lamp to various uses, it becomes important to obtain white light especially with one LED lamp. Then, to take out white light from one LED lamp is tried by applying blue, green, and a red light fluorescent substance on the surface of a LED tip, or making the phosphor powder of each color luminescence contain in the resin which constitutes LED. These days, since color sense becomes rich and delicate tone (color reproduction nature) has come to be required also of various displays, to take out luminescence of not only white light but arbitrary neutral colors from one LED lamp is tried.
[0004]In a LED lamp which was described above, the LED tip (for example, LED tip which has a GaN system compound semiconductor layer as a luminous layer) which emits ultraviolet A with a wavelength of around 370 nm as a light source is used. For this reason, the ultraviolet rays of long wavelength which was described above are well absorbed to the fluorescent substance used for a LED lamp, and it is asked for what emits light in visible light efficiently.
[0005]By the way, it had become a problem that a red light fluorescent substance has weak absorption of ultraviolet A with a wavelength of around 370 nm compared with the fluorescent substance of other luminescent color (blue and green) among the fluorescent substances of each color luminescence excited by ultraviolet A. To such a point, to JP,11-246857,A. The acid lanthanum sulfide (La_2O_2S:Eu, Sm) fluorescent substance activated with trivalent europium (Eu) and samarium (Sm), Ultraviolet A with a wavelength of around 370 nm is absorbed efficiently, and it is indicated that the red light near 625 nm is efficiently obtained for peak wavelength by this.
[0006]
[Problem(s) to be Solved by the Invention]As mentioned above, the acid lanthanum sulfide (La_2O_2S:Eu, Sm) fluorescent substance activated by trivalent Eu and Sm, Since ultraviolet A with a wavelength of around 370 nm is absorbed efficiently and peak wavelength emits light efficiently in the red light near 625 nm, it is expected as a red light fluorescent substance used for a LED lamp etc.
[0007]However, from having some hygroscopicity, when above-mentioned La_2O_2S:Eu and Sm fluorescent substance are kept for a long period of time, for example, they have the problem of being easy to condense a fluorescent substance particle. If the fluorescent substance particle of red light condenses, when producing the LED lamp of white light, for example, phosphor powder of red light will not be able to be uniformly distributed in resin, and, thereby, nonuniformity will arise from a LED lamp to luminescence. That is, variation arises in the color temperature of the white light which emits light from a LED lamp, and this has become a debasement factor of the LED lamp.
[0008]When it is made in order to cope with such a technical problem, and it excites, for example by ultraviolet A, after red light harnesses the feature of La_2O_2S:Eu obtained efficiently and Sm fluorescent substance, this invention, By preventing the condensation by the moisture absorption at the time of storage, etc., aiming at providing the red light fluorescent substance which made it possible to hold good dispersibility over a long period of time, and using still such a red light fluorescent substance, It aims at providing the luminescent device which has improved a luminescent characteristic and manufacturability.
[0009]

[Means for Solving the Problem]This invention is characterized by a red light fluorescent substance comprising the following.
A fluorescent substance particle which consists of an acid lanthanum sulfide fluorescent substance activated with trivalent europium and samarium as indicated to claim 1.
A damp proof course which consists of a metallic oxide to which the surface of said fluorescent substance particle adhered.

[0010]As indicated, for example to claim 2, an acid lanthanum sulfide fluorescent substance used by this invention, General formula: $(La_{1-x-y}Eu_xSm_y)$ It has the presentation expressed with $_2O_2S$ (the inside of a formula, and x and y are 0.01<=x<=0.15 and a number with which it is satisfied of 0.0001<=y<=0.03, respectively).
[0011]In a red light fluorescent substance of this invention, a damp proof course which consists of metallic oxides is formed in the surface of a fluorescent substance particle which consists of trivalent europium and a samarium activation acid lanthanum sulfide fluorescent substance which absorb efficiently ultraviolet rays of long wavelength with a wavelength of around 370 nm, for example, and emit light efficiently in red light. A damp proof course which consists of metallic oxides prevents a fluorescent substance particle absorbing moisture, and it has a function which raises the dispersibility of a fluorescent substance particle. After maintaining the luminescent characteristic of a fluorescent substance particle which consists of trivalent europium and a samarium activation acid lanthanum sulfide fluorescent substance by such a damp proof course, condensation of a fluorescent substance particle is controlled and it becomes possible to hold good dispersibility over a long period of time.
[0012]As what is excellent in a metallic oxide which constitutes a damp proof course in a red light fluorescent substance of this invention at dampproofing, and does not have a luminescent characteristic substantially was used and specifically being indicated to claim 3, It is preferred to use an oxide containing at least one sort of metallic elements chosen from aluminum, Si, Y, Gd, Lu, Ti, Nb, Ta, and Zn. As for a metallic oxide, as indicated to claim 4, it is preferred to make it adhere in 0.01 to 5% of range in a mass ratio to a fluorescent substance particle.
[0013]As indicated a red light fluorescent substance of this invention to claim 6, when it excites by ultraviolet rays with a wavelength of 270-395 nm, it emits light in red light. Especially a red light fluorescent substance of this invention is excellent in luminous efficiency of red light at the time of exciting by ultraviolet A with a wavelength of 350-390 nm, as indicated to claim 7.
[0014]This invention is characterized by a luminescent device comprising the following.
A light source which emits ultraviolet rays as indicated to claim 8.
A light-emitting part which has a fluorescent substance for luminescent devices which is excited by ultraviolet rays from said light source, and makes visible light emit light, including a red light fluorescent substance of above-mentioned this invention.

[0015]In a luminescent device of this invention, as indicated to claim 9, the above-mentioned light-emitting part can be added to a red light fluorescent substance of this invention, and can use a fluorescent substance for luminescent devices containing a blue light fluorescent substance and a green emission fluorescent substance. As an example of a luminescent device of this invention, as indicated to claim 10, a LED lamp possessing a light emitting chip which has a nitride based compound semiconductor layer which emits ultraviolet A with a wavelength of 350-390 nm as a light source, etc. are mentioned.
[0016]
[Embodiment of the Invention]Hereafter, the gestalt for carrying out this invention is explained.
[0017]Drawing 1 is a sectional view showing typically the composition of the red light fluorescent substance by one embodiment of this invention. The red light fluorescent substance 1 shown in the figure has the fluorescent substance particle 2 which consists of an acid lanthanum sulfide (La_2O_2S) fluorescent substance activated with trivalent europium (Eu) and samarium (Sm).
[0018]The acid lanthanum sulfide fluorescent substance which constitutes the fluorescent substance particle 2, For example, a general formula: $(La_{1-x-y}Eu_xSm_y)_2O_2S$ -- It has the

presentation expressed substantially [(1) and / (the inside of a formula, and x and y are 0.01<=x<=0.15 and a number with which it is satisfied of 0.0001<=y<=0.03, respectively)].
[0019]Here, trivalent europium (Eu) is an activator which raises the luminous efficiency of the acid lanthanum sulfide as a fluorescent substance parent, and it is preferred to make it contain in 0.01-0.15 as a value of x of the above-mentioned (1) formula. There are few improvement effects of luminous efficiency that the value of x which shows the content of Eu is less than 0.01, and there is a possibility that sufficient luminosity cannot be obtained. On the other hand, if the value of x exceeds 0.15, luminosity will fall by concentration quenching etc. As for the value of x, it is still more preferred to consider it as the range of 0.03-0.08.
[0020]Samarium (Sm) has the operation which shifts the excitation spectrum of the fluorescent substance which it functions as an activator and also uses an acid lanthanum sulfide as a parent to the long wavelength side. The absorption efficiency of ultraviolet A with a wavelength of 350-390 nm is improved by this, for example, and the luminous efficiency at the time of exciting by such ultraviolet A can be raised by it. As for Sm, it is preferred to make it contain in 0.0001-0.03 as a value of y of (1) type. There is a possibility that the effect of shifting excitation-spectrum wavelength to the long wavelength side as the value of y is less than 0.0001 may not fully be acquired. On the other hand, when the value of y exceeds 0.03, the luminous efficiency of a fluorescent substance will be checked conversely. As for the value of y, it is still more preferred to consider it as the range of 0.001-0.01.
[0021]In the acid lanthanum sulfide as a fluorescent substance parent, Y, Gd, or Y+Gd may replace some lanterns (La) with at least one sort of elements and the concrete target which are chosen from yttrium (Y) and gadolinium (Gd). By dissolving in a fluorescent substance, Y and Gd show the effect which raises the emitted energy in a red spectrum region. However, as for the amount of substitution by Y or Gd, since it will become impossible to disregard distortion of a crystal and luminescence intensity will fall conversely if there are too many amounts of substitution of La by Y or Gd, it is preferred to use less than 30 mol % of La. The more desirable amount of substitution is 5-20-mol% of the range.
[0022]Trivalent Eu and Sm activation acid lanthanum sulfide fluorescent substance which constitute the fluorescent substance particle 2 absorb efficiently ultraviolet rays with a wavelength of 270-395 nm, especially ultraviolet A with a wavelength of 350-390 nm. Therefore, when it excites by such ultraviolet rays (especially ultraviolet A), peak wavelength can obtain the red light near 625 nm efficiently, and is useful as a red light fluorescent substance for various displays, etc., for example.
[0023]And in the red light fluorescent substance 1 of this invention, the metallic oxide to which the metallic oxide was made to adhere to the surface of the fluorescent substance particle 2 which consists of above-mentioned trivalent Eu and acid lanthanum sulfide fluorescent substance of Sm activation, and the surface of this fluorescent substance particle 2 adhered forms the damp proof course 3.
[0024]The stability of itself and dampproofing are high to the metallic oxide which constitutes the damp proof course 3, and the oxide which does not have a luminescent characteristic substantially is used for it. It is preferred to use the oxide which the oxide containing the metallic element chosen from aluminum, Si, Y, Gd, Lu, Ti, Nb, Ta, and Zn is illustrated, and contains one or more sorts of these metallic elements as such a metallic oxide.
[0025]that the damp proof course 3 which consists of metallic oxides makes the particles of a metallic oxide adhere to the surface of the fluorescent substance particle 2 for example **** -- the surface of the fluorescent substance particle 2 -- the tunic (the thing of the shape of an approximately tunic by an ultrafine particle layer etc. is included) of a metallic oxide -- a wrap -- it is formed of things. When the red light fluorescent substance 1 is kept for a long period of time, for example by forming such a damp proof course 3 in the surface of the fluorescent substance particle 2, it becomes possible to prevent the fluorescent substance particle 2 absorbing and condensing moisture.
[0026]As described above, since the damp proof course 3 which consists of metallic oxides has a function which prevents a fluorescent substance particle from absorbing moisture 2, it can control certainly condensation of the fluorescent substance particle 2 after storage, for example.

The metallic oxide as the damp proof course 3 acts effectively also to improvement in the dispersibility of the fluorescent substance particle 2.
[0027]When producing a LED lamp etc. using the red light fluorescent substance 1 of this invention based on a condensation preventive effect, a dispersibility improved effect, etc. of such a damp proof course 3, it becomes possible to distribute the red light fluorescent substance 1 uniformly in resin after long term storage. Therefore, a LED lamp without emission unevenness and a LED lamp with a uniform color temperature of luminescence by putting in another way can be provided. Such an upgrading effect of a LED lamp can be especially acquired notably, when mixing the red light fluorescent substance 1 of this invention with blue and a green emission fluorescent substance and producing the LED lamp of white light using such a mixed fluorescent substance.
[0028]As for the damp proof course 3 which was mentioned above, it is preferred to make the metallic oxide which constitutes it adhere in 0.01 to 5% of range, and to form it with a mass ratio, to the fluorescent substance particle 2. There is a possibility that a condensation preventive effect, a dispersibility improved effect, etc. which were described above to the fluorescent substance particle 2 as the coating weight of a metallic oxide is less than 0.01 mass % cannot fully be acquired. On the other hand, since the damp proof course 3 is what bars luminescence of the fluorescent substance particle 2 fundamentally, if the coating weight of such a metallic oxide exceeds 5 mass %, the fall of the radiant power output of the red light fluorescent substance 1 will become remarkable, and practicality will fall. As for the coating weight to the fluorescent substance particle 2 of a metallic oxide, it is more preferred to consider it as 0.05 to 1% of range with a mass ratio. The kind and quantity of a metallic oxide in this invention are measured by ICP emission spectrometry. However, when Y or Gd is contained in a hardener, it measures by EPMA.
[0029]The damp proof course 3 which consists of metallic oxides can be formed with a particle method, a solution technique, etc. which are shown below, for example. In a particle method, the impalpable powder of a metallic oxide is distributed underwater first, an organic high polymer system binder etc. are added trivalent Eu and Sm activation acid lanthanum sulfide phosphor powder, and also if needed into these dispersion liquid, and it fully agitates. After filtering this suspension, by carrying out stoving, the damp proof course 3 which consists of metallic oxides can be formed in the surface of the fluorescent substance particle 2 which consists of trivalent Eu and an acid lanthanum sulfide fluorescent substance of Sm activation. According to such a particle method, a metal oxide particle adheres to the surface of the fluorescent substance particle 2, and the damp proof course 3 is formed.
[0030]In a solution technique, water soluble compounds containing metallic elements (aluminum, Si, Y, Gd, Lu, Ti, Nb, Ta, Zn, etc.) which were described above, such as a nitrate and carbonate, are dissolved underwater, trivalent Eu and the acid lanthanum sulfide phosphor powder of Sm activation are added into this solution, and it fully agitates. By heat-treating the filtration cake obtained by performing pH adjustment of this mixed solution, etc., generating gel hydroxide etc., and filtering after further fully agitating in this state, The damp proof course 3 which consists of metallic oxides can be formed in the surface of the fluorescent substance particle 2 which consists of trivalent Eu and an acid lanthanum sulfide fluorescent substance of Sm activation. according to such a solution technique -- the surface of the fluorescent substance particle 2 -- a metallic-oxide tunic (or ultrafine particle layer) -- a wrap -- things are made.
[0031]The red light fluorescent substance 1 of this invention which was mentioned above is suitably used as a use which excites, for example by ultraviolet rays with a wavelength of 270-395 nm, especially ultraviolet A with a wavelength of 350-390 nm, and obtains visible light, for example, a fluorescent substance for luminescent devices. And the luminescent device of this invention constitutes the red light fluorescent substance 1 of such this invention using the fluorescent substance for luminescent devices included at least.
[0032]The luminescent device of this invention irradiates with the ultraviolet rays of long wavelength, etc. the light-emitting part which has a fluorescent substance for luminescent devices which contains at least the red light fluorescent substance 1 of this invention mentioned above from various kinds of light sources, and it constitutes them so that this may obtain visible

light from a light-emitting part. Although a LED lamp is mentioned as an example of representation of such a luminescent device, it is also applicable to for example, the display for signs (luminescent device), etc. besides this.
[0033]Drawing 2 is a sectional view showing the outline composition of one embodiment which applied the luminescent device of this invention to the LED lamp. In the figure, the center wavelength in which 11 has for example, an InGaN active layer is an ultraviolet LED tip near 370 nm, and this ultraviolet LED tip 11 is being fixed via the adhesives layer 13 on the leadframe 12. Ultraviolet LED tip 11 and the leadframe 12 are electrically connected by the bonding wire 14.
[0034]Ultraviolet LED tip 11 is covered with the resin layer 15 with the bonding wire 14 etc. Here, the resin layer 15 has [the circumference of ultraviolet LED tip 11] the wrap casting material 17 for the circumference of the wrap pre dip material 16 and this pre dip material 16. Transparent resin etc. are used for the pre dip material 16 and the casting material 17.
[0035]In the LED lamp shown in drawing 2, the pre dip material 16 contains the fluorescent substance for luminescent devices which contains at least the red light fluorescent substance of this invention mentioned above, It is excited by the ultraviolet rays emitted from ultraviolet LED tip 1, and functions as a light-emitting part which makes the visible light according to a kind, the mixing ratio, etc. of the fluorescent substance for luminescent devices emit light. The fluorescent substance for luminescent devices is not restricted to using it, making it contain in the pre dip material 16, and can be used with various gestalten, such as forming and using a fluorescent substance layer for the light-emitting surface of ultraviolet LED tip 11, for example.
[0036]According to the luminescent color made into the purpose, in addition to the red light fluorescent substance of this invention, the fluorescent substance for luminescent devices can mix a blue light fluorescent substance, a green emission fluorescent substance, etc., and can be used. Under the present circumstances, since it excels in dispersibility, when mixing with blue, a green emission fluorescent substance, etc. and making it distribute in the pre dip material 16, after the red light fluorescent substance of this invention maintains the good mixed state, uniform dispersion of it can be carried out. This enables it to control generating of emission unevenness, etc.
[0037]In the fluorescent substance for luminescent devices mentioned above, although each fluorescent substance in particular as a blue light ingredient and a green emission ingredient is not limited, it is preferred to use the fluorescent substance which is excellent in the luminous efficiency by the ultraviolet rays of long wavelength.
[0038]For example, as a blue light fluorescent substance, they are general formula:$(M1, Eu)_{10}(PO_4)_6Cl_2$ (among a formula). at least one sort of elements in which M1 is chosen from Mg, Ca, Sr, and Ba -- being shown -- the divalent europium activation halo phosphate fluorescent substance with which it is expressed substantially. And a general formula: $a(M2, Eu)O-bAl_2O_3$ (among a formula) M2 shows at least one sort of elements chosen from Mg, Ca, Sr, Ba, Zn, Li, Rb, and Cs, the number with which a and b are satisfied of $a>0$, $b>0$, and $0.2<=a/b<=1.5$ -- it is -- it is preferred to use at least one sort chosen from the divalent europium activation aluminate phosphor expressed substantially.
[0039]As a green emission ingredient, it is general formula:$c(M2, Eu, Mn)O-dAl_2O_3$ (among a formula). M2 shows at least one sort of elements chosen from Mg, Ca, Sr, Ba, Zn, Li, Rb, and Cs, the number with which c and d are satisfied of $c>0$, $d>0$, and $0.2<=c/d<=1.5$ -- it is -- divalent europium and the manganese activation aluminate phosphor which are expressed substantially. And a general formula: $(Y_{1-v-w-z}R_vTb_wCe_z)_2O_3$ and $nSiO_2$ (among a formula) R is shown and at least one sort of elements chosen from La and Gd v, w, the number with which z and n are satisfied of $5x10^{-4}<=v<=0.3$, $0.05<=w<=0.3$, $0.001<=z<=0.15$, and $0.8<=n<=1.3$, respectively -- it is -- at least one sort chosen from the trivalent terbium and cerium activation rare earth silicate phosphor which are expressed substantially. Using is preferred.
[0040]Each of blue which was described above, and green emission fluorescent substances is excellent in the absorption efficiency of ultraviolet rays with a wavelength of 270-395 nm, especially ultraviolet A with a wavelength of 350-390 nm, and when it excites [therefore] by

the ultraviolet rays of long wavelength, they can obtain blue glow and green light efficiently. By using it, combining as suitably as the red light fluorescent substance of this invention such blue, a green emission fluorescent substance, etc., neutral-colors lights, such as the arbitrary white light of a color temperature and purple, pink, and blue-green, can be taken out efficiently, and it becomes possible to raise the color reproduction nature of each color substantially further.
[0041]The mixing ratio of red and each blue and green color luminescent components can be suitably set up according to the luminescent color made into the purpose. For example, when acquiring white light, it is preferred to make a green emission ingredient into 5 to 65% of range, and to make a red light ingredient into 15 to 95% of range for a blue light ingredient 65% or less, with a mass ratio. According to such the mixing ratio, color temperature 2700K to 8000K order white light can be acquired arbitrarily, for example, and a luminosity without the three-wave fluorescent substance excited on the further conventional wavelength of 254 nm and inferiority is obtained.
[0042]The luminescent device of this invention is not restricted to the LED lamp mentioned above, and can be applied to the display possessing the light-emitting part which applied with the paint the fluorescent substance for luminescent devices which contains the red light fluorescent substance of this invention, for example, and the light source which irradiates this light-emitting part with ultraviolet rays, especially ultraviolet A, etc. Such a display is used for a sign etc., As a light source in that case, it is $BaSi_2O_5$:P The black light (fluorescent lamp) using b fluorescent substance (peak wavelength: 353 nm), a SrB_4O_7:Eu fluorescent substance (peak wavelength: 370 nm), etc. is used.
[0043]
[Example]Next, the concrete example of this invention and its evaluation result are described.
[0044]Example 1 and the comparative example 1 -- first 0.74 g of nitric acid yttrium ($Y(NO_3)_3$) to the pure water 0.2L (liter), [dissolve and] Trivalent Eu and Sm activation acid lanthanum sulfide fluorescent substance ($(La_{0.93}Eu_{0.06}Sm_{0.01})_2O_2S$) powder 100g were added in this solution, and it fully agitated in it. Subsequently, the ammonia solution was dropped agitating to these dispersion liquid, and the pH of dispersion liquid was adjusted to around nine. The gel material of hydroxylation yttrium is obtained in this pH range. Pure water washed, after further fully agitating in this state. The red light fluorescent substance made into the purpose was obtained by heat-treating the filtration cake obtained by carrying out suction filtration of this suspension on the conditions of 400 **x 6 hours.
[0045]Thus, in the obtained red light fluorescent substance, stick forming of the Y_2O_3 ultrafine particle layer was carried out to the surface of La_2O_2S:Eu and Sm fluorescent substance particle. It checked by SEM that this Y_2O_3 ultrafine particle layer had become tunic-like about. The coating weight of La_2O_2S:Eu and Y_2O_3 to Sm fluorescent substance particle was 0.2 mass %.

[0046]The red light fluorescent substance by the above-mentioned Example 1, and except not forming the metal oxide layer in a fluorescent substance particle surface, after neglecting these in various time in the atmosphere using the same red light fluorescent substance (comparative example 1) as Example 1, the state of aggregation of each fluorescent substance was evaluated as follows. The result is shown in Table 1.
[0047]Cohesiveness evaluation of the fluorescent substance was carried out as follows. First, 40 cc of xylene solutions which dissolved 1.5% of ethyl cellulose are put in in a glass tube 15 mm in inside diameter, and 300 mm in height. 20 g of phosphor powder is put in this, a glass tube is often shaken for 20 minutes, and uniform suspension is prepared. Then, after holding a glass tube vertically and neglecting it for 48 hours, the height of the fluorescent substance layer which sedimented is measured. Whenever it makes into a standard (ten points) the height of the red light fluorescent substance of this invention neglected in the atmosphere for one day and height increases it 1.15 times, the state of aggregation of a fluorescent substance is evaluated as one minus. If a fluorescent substance condenses, the dispersibility in the inside of carrier fluid will

worsen, and the height of the fluorescent substance layer which sedimented as the result becomes high.

[0048]

[Table 1]

	凝集状態評価点				
放置日数	1日	10日	30日	90日	180日
実施例1	10	10	10	10	10
比較例1	9	9	7	6	5

[0049]It turns out that it is hardly condensed after keeping the red light fluorescent substance by Example 1 in the atmosphere for a long time, but good dispersibility is maintained from this so that clearly from Table 1.

[0050]Example 2 and the comparative example 2 — first, aluminum oxide (aluminum$_2O_3$) impalpable powder with a particle diameter of around 50 nm was added to the pure water 0.2L (liter), and it fully agitated to it. In these dispersion liquid, trivalent Eu and Sm activation acid lanthanum sulfide fluorescent substance ($La_{0.90}Eu_{0.07}Sm_{0.03}$) ($_2O_2S$) powder 100g were added, and it further fully agitated. Subsequently, after adding one by one and distributing uniformly a 0.1-g acrylic emulsion and 0.05 g of polyacrylic acid ammonium, the red light fluorescent substance made into the purpose was obtained by drying the filtration cake obtained by filtering this suspension on the conditions of 120 **x 24 hours.

[0051]Thus, in the obtained red light fluorescent substance, aluminum$_2O_3$ particles had adhered to the surface of La_2O_2S:Eu and Sm fluorescent substance particle, and it checked by SEM that the aluminum$_2O_3$ particle layer was formed. The coating weight of La_2O_2S:Eu and aluminum$_2O_3$ to Sm fluorescent substance particle was 0.5 mass %.

[0052]The red light fluorescent substance by the above-mentioned Example 2, and except not forming the metal oxide layer in a fluorescent substance particle surface, after neglecting these in various time in the atmosphere using the same red light fluorescent substance (comparative example 2) as Example 2, the state of aggregation of the fluorescent substance as well as Example 1 was evaluated. The result is shown in Table 2.

[0053]

[Table 2]

	凝集状態評価点				
放置日数	1日	10日	30日	90日	180日
実施例2	10	10	10	9	9
比較例2	9	9	7	6	5

[0054]It turns out that it is hardly condensed after keeping the red light fluorescent substance by Example 2 in the atmosphere for a long time, but good dispersibility is maintained from this so that clearly from Table 2.

[0055]After making the metallic oxide shown in Table 3, respectively adhere like Example 2 to trivalent Eu and Sm activation acid lanthanum sulfide fluorescent substance which show a presentation in the three to Examples 3-9 and comparative example 9 table 3, the state of aggregation after storage of these each red light fluorescent substance was evaluated like Example 1. The result is shown in Table 4. The comparative examples 3-9 in front are the same red light fluorescent substances as Examples 3-9 except not forming the metal oxide layer in a fluorescent substance particle surface.

The state of aggregation after storage was evaluated also about these.

[0056]

[Table 3]

	蛍光体粒子（組成）	金属酸化物	
		組成	付着量（質量%）
実施例3	$(La_{0.899}Eu_{0.10}Sm_{0.001})_2O_2S$	SiO_2	1.0
比較例3	$(La_{0.899}Eu_{0.10}Sm_{0.001})_2O_2S$	—	—
実施例4	$(La_{0.8499}Eu_{0.15}Sm_{0.0001})_2O_2S$	TiO_2	5.0
比較例4	$(La_{0.8499}Eu_{0.15}Sm_{0.0001})_2O_2S$	—	—
実施例5	$(La_{0.79}Y_{0.10}Eu_{0.10}Sm_{0.01})_2O_2S$	ZnO	0.05
比較例5	$(La_{0.79}Y_{0.10}Eu_{0.10}Sm_{0.01})_2O_2S$	—	—
実施例6	$(La_{0.70}Gd_{0.20}Eu_{0.08}Sm_{0.02})_2O_2S$	Gd_2O_3	3.0
比較例6	$(La_{0.70}Gd_{0.20}Eu_{0.08}Sm_{0.02})_2O_2S$	—	—
実施例7	$(La_{0.989}Eu_{0.01}Sm_{0.001})_2O_2S$	Ta_2O_5	0.01
比較例7	$(La_{0.989}Eu_{0.01}Sm_{0.001})_2O_2S$	—	—
実施例8	$(La_{0.879}Eu_{0.12}Sm_{0.001})_2O_2S$	Nb_2O_5	0.5
比較例8	$(La_{0.879}Eu_{0.12}Sm_{0.001})_2O_2S$	—	—
実施例9	$(La_{0.94}Eu_{0.05}Sm_{0.01})_2O_2S$	Lu_2O_3	0.1
比較例9	$(La_{0.94}Eu_{0.05}Sm_{0.01})_2O_2S$	—	—

[0057]
[Table 4]

	凝集状態評価点				
放置日数	1日	10日	30日	90日	180日
実施例3	10	10	10	10	9
比較例3	9	9	6	6	5
実施例4	10	10	10	10	10
比較例4	9	9	7	6	5
実施例5	10	10	10	10	9
比較例5	9	9	8	6	5
実施例6	10	10	10	10	10
比較例6	9	9	7	6	5
実施例7	10	10	10	9	9
比較例7	9	9	8	6	6
実施例8	10	10	10	10	9
比較例8	9	9	8	7	5
実施例9	10	10	10	10	9
比較例9	9	9	7	6	5

[0058]It turns out that it is hardly condensed after keeping each red light fluorescent substance by Examples 3-9 in the atmosphere for a long time, but good dispersibility is maintained from this so that clearly from Table 4.
[0059]Example 10 and the comparative example 10 — first with the red light fluorescent substance by Example 1, and the blue light fluorescent substance of $_{10}(Sr_{0.73}Ba_{0.22}Ca_{0.05})(PO_4)_6$ and a Cl_2:Eu presentation. The green emission fluorescent substance of the 3(Ba, Mg) Oand8aluminum$_2O_3$:$Eu_{0.20}$ and $Mn_{0.40}$ presentation was prepared. The color temperature obtained the 6500K order white light fluorescent substance by a red light ingredient's carrying out weighing of the fluorescent substance of these each color with a mass ratio, so that a blue light ingredient will be 21% and a green emission ingredient may be 18% 61%, and fully mixing these. The red light fluorescent substance used the thing after keeping it for 90 days.
[0060]Thus, the LED lamp shown in drawing 2 was produced using the obtained mixed fluorescent substance. The LED lamp was produced by specifically distributing the above-mentioned mixed fluorescent substance in the epoxy resin solution as the pre dip material 6, and covering the circumference of the ultraviolet LED tip which has an InGaN active layer using this resin solution. In the making process of this LED lamp, it checked distributing the above-mentioned mixed fluorescent substance uniformly in a resin solution. When the lighting examination of the LED lamp was done, generating of emission unevenness was not accepted but it checked that white light with a uniform color temperature was acquired.

[0061]Except on the other hand, using it, after keeping the red light fluorescent substance by the comparative example 1 for 90 days as the comparative example 10 with this invention, When the LED lamp was produced like the above-mentioned Example 10, generating of emission unevenness was observed in the LED lamp obtained by accepting separation of a fluorescent substance by the dispersing process to the inside of the resin solution of a mixed fluorescent substance.
[0062]
[Effect of the Invention]As explained above, after harnessing the feature of La_2O_2S:Eu of excelling in the luminous efficiency of the red light at the time of exciting, for example by ultraviolet A, and Sm fluorescent substance according to the red light fluorescent substance of this invention, The condensation by the moisture absorption at the time of storage, etc. can be prevented, and it becomes possible to hold good dispersibility over a long period of time. Therefore, it becomes possible by using such a red light fluorescent substance to aim at the characteristic of a luminescent device and the improvement in quality which make ultraviolet A an excitation source, for example.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a sectional view showing typically the composition of the red light fluorescent substance by one embodiment of this invention.
[Drawing 2]It is a sectional view showing the outline composition of one embodiment which applied the luminescent device of this invention to the LED lamp.
[Description of Notations]
1 [.... An ultraviolet LED tip, 15 / ---- A resin layer, 16 / ---- Pre dip material] .... A red light fluorescent substance, 2 .... A fluorescent substance particle, 3 .... A damp proof course, 11

[Translation done.]

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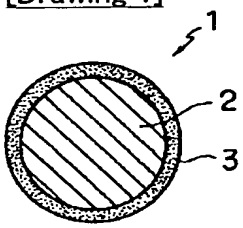
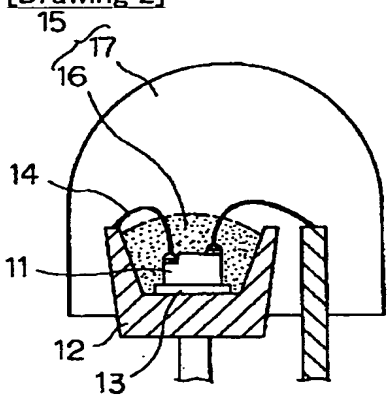
DRAWINGS

[Drawing 1]



[Drawing 2]



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